



## An Approach to High Resolution *Ex-Situ* NMR

Alex Pines and coworkers have made a major advance toward the realization of high resolution nuclear magnetic resonance (NMR) spectroscopy of samples in the nonuniform magnetic field found outside the bore of the spectrometer magnet. The work was described in the July 6, 2001 issue of *Science*.

NMR spectroscopy is widely used by scientists to study the molecular structure and chemical dynamics of a vast range of compounds, materials, and processes. In order to attain high resolution, the studies must be performed in the strong and highly uniform magnetic field that is found inside the bore of a very large stationary magnet. Under these conditions, those nuclei in the sample that have magnetic moments (e.g. hydrogen) align their spins either “up” or “down” with respect to the direction of the applied magnetic field. When the sample is irradiated with a radio-frequency (rf) pulse that matches the slight energy difference between the up and down spins, the nuclei begin to precess (wobble) on a tilted axis around the magnetic field lines. In time, the nuclei relax and realign themselves with the static field by emitting rf radiation at an energy corresponding to their precession frequency. Because the rate at which the nuclei precess depends on their local chemical environment, the spectrum of the emitted rf radiation contains information about the chemical structure of the sample. For example, signals from different hydrogen nuclei in organic compounds appear as distinct peaks in an NMR spectrum depending on their position in the molecule (see figure).

It would be highly desirable to achieve “*ex-situ* NMR” spectroscopy of samples that cannot physically be placed inside the magnet. This would be useful in numerous applications, including oil field exploration, where it could be used to distinguish oil from water; and studies of the surface of materials, where an NMR probe could be scanned across, for example, a microarray of samples in an assaying application. Unfortunately, in the non-uniform field outside the magnet, nuclei with identical chemical environments will precess faster (or slower) depending on whether they are in a region of stronger (or weaker) magnetic field. This results in a broad spectrum of re-emitted radiation and the loss of all chemical information (see figure).

In a new approach to this problem, the Pines group developed a method to use carefully chosen sequences of rf pulses to “refocus” the precessing nuclei of samples in the nonuniform field outside rf coil. The method reverses the order of precession of the “fast” and “slow” nuclei such that the “slower” nuclei can catch up to the “faster” ones. By detecting the signal at just the moment when all the nuclei are realigned, high resolution data can be recovered (see figure). Initial studies involved simple organic compounds. The group is now working on combining their new method with the existing technique of “magic angle spinning” in order to study heterogeneous materials under *ex-situ* conditions. Potential applications include scanning micro-tip NMR of surfaces, microarrays, microchips; *ex-situ* NMR for, e.g., oil exploration; and *ex-situ* (out-of-the magnet bore) medical MRI.

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Carlos A. Meriles, Dimitris Sakellariou, Henrike Heise, Adam J. Moule, Alexander Pines, “Approach to High-Resolution *ex-Situ* NMR Spectroscopy,” *Science* 293, 82 (2001).